

SELECTIVE PLATING OF NICKEL CERAMIC COMPOSITE FILMS FOR MEMS APPLICATIONS

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ABSTRACT

A simple, selective and CMOS-compatible deposition method for nickel ceramic composite film has been demonstrated. Using electroless plating technique, two types of nickel ceramic composite thin films, nickel-cordierite and nickel-iron (II, III) oxide, have been successfully deposited and characterized on silicon substrates. The incorporation of an appropriate amount of cordierite particles into a nickel matrix is shown to significantly reduce the thermal expansion mismatch between nickel and silicon, yet maintain the Young's modulus, Berkovich hardness and electrical resistivity at approximately 167 GPa, 7.6 GPa and 9.4 mW-cm, respectively, which correspond closely to electroless nickel. On the other hand, the addition of iron (II, III) oxide instead of cordierite can also increase the coercivity of electroless nickel up to 170 Oe, thereby significantly enhances its ferromagnetic property.

Key words: Electroless plating, nickel ceramic composite

INTRODUCTION

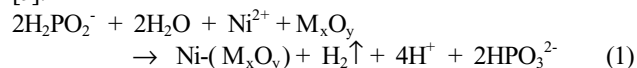
As MEMS enters the commercialization phase, massively parallel manufacturability, ease of integration with other components and precise control of material properties become the most important issues to contend with. Furthermore, the ability to integrate CMOS circuitry concurrently with MEMS structures will benefit the development of commercial product. Hitherto, polysilicon has been the workhorse material for MEMS due to its superior mechanical properties and the well-established fabrication technologies from the IC industry. However, the high thermal budget of most polysilicon processes complicates the concurrent fabrication of CMOS circuitry, which is not cost effective for the commercialization of many polysilicon MEMS. Besides, the low deposition rate of polysilicon also hinders its applications for high aspect ratio MEMS. In contrast, electroplated nickel has comparable mechanical properties with polysilicon, lower resistivity, higher deposition rate and lower processing temperature which make it an alternative material for MEMS, and especially for high aspect ratio structures [1]. Nevertheless, thermal stress generated by large thermal expansion mismatch between nickel and silicon renders electroplated nickel to be an unsuitable candidate for high-performance and high-precision CMOS-based integrated microsystem applications.

One method to circumvent this challenge, from the standpoint of material science, is to selectively modify the properties of the nickel thin film to match that of the substrate.

Previous studies have shown that the physical properties of a particular material can be engineered to match that of another via the addition of an appropriate quantity of the latter material [2]. For example, particulate inclusion is one way to increase the mechanical toughness through the dispersion of second-phase particles in a ductile metal matrix [3,4]. Hence, It can be expected that incorporating fine second phase particles, such as ceramic particles, polymer, magnetite or even diamond, into a nickel film during an electroplating process can modify the physical properties of nickel film such as the thermal expansion coefficient (CTE), ferromagnetic property or even the ratio of Young's modulus to density. In this paper, we introduce a simple, selective and CMOS-compatible electroless plating process for depositing conductive nickel ceramic thin films. This technique also offers reliable control of film growth, low processing temperature and low fabrication cost.

ELECTROLESS NICKEL CERAMIC PLATING PROCESS

Electroless nickel ceramic plating is a process that facilitates the formation of a nickel coating, which contains fine ceramic particles on the catalytically activated surface of a substrate [5]. In this experiment, a commercially available acidic nickel plating bath is used. It contains additives such as a brightener, and a stabilizer to prevent self-decomposition of the solution. Figure 1 shows the deposition process of the nickel-ceramic composite film on a silicon substrate, which has a 500Å thick copper film sputtered on top. This substrate is first immersed in a Pd seeding solution for up to 4 minutes for surface chemistry modification. Pd ions will physically adhere only onto the copper surface, and they catalyze the following redox reaction once the wafer is immersed in the plating bath [5]:



The nickel plating bath where the above reaction takes place is a stable colloidal system that has ceramic particles (M_xO_y), either in the form of cordierite, or iron (II,III) oxide, well-dispersed within. The particle concentration and particle size can be pre-determined to produce desirable film properties. The particle sizes used in these experiments range from tens of nm up to 5µm, and the concentration has been kept at 10g per liter of Ni plating solution. While nickel is precipitated out of the solution onto the catalytic surface of the substrate, ceramic particles drifting in the solution will come into contact with the growing nickel film and stick onto it momentarily. Some large ceramic particles will eventually drift away as a result of the convective current in the solution, others will remain adhered

onto the surface and slowly be engulfed by the thickening nickel film. Finally, a nickel film that is composed of dispersed second phase particles will be formed.

The plating rate is highly dependent not only on the temperature, but also on the pH of the solution. At a plating temperature of 78°C and the pH of 4, the plating rates of the composite films can be up to 10µm/hr, which is close to the plating rate of pure electroless nickel. Equation (1) shows that the presence of an excess concentration of protons will favor the reverse reaction based on the Le Chatelier's Principle. It is therefore necessary to maintain the concentration of the plating bath by constantly monitoring the pH level of the bath.

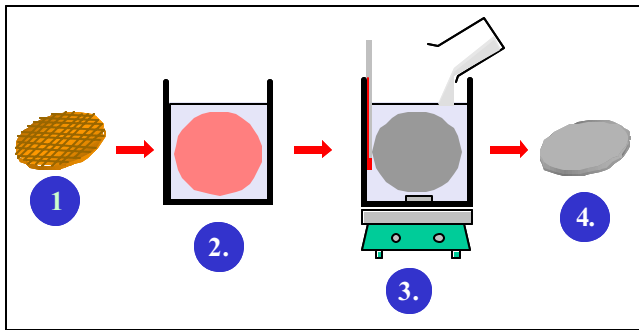


Figure 1. Steps in electroless plating of metal-ceramic composite thin film include: 1. Start with a copper-coated wafer (500Å); 2. Immerse wafer in a palladium (Pd) solution for 4 minutes of seeding; 3. Transfer seeded wafer into a metal plating bath well-mixed with ceramic particles and maintained at 78°C; 4. Remove wafer coated with metal-ceramic composite thin film after desirable thickness is achieved.

PLATING RESULTS AND DISCUSSIONS

Figure 2 shows the SEM of a 5 µm thick nickel-cordierite film after 30 minutes of deposition, and Figure 3 is an Electron Dispersion XRay (EDXTM) graph that indicates the relative amount of various elements in addition to nickel in the film. Figure 2 shows that, the large cordierite particle aside, the smaller cordierite particles have been distributed within the nickel matrix. The existence of large particles of sizes comparable to the film thickness underlines the importance of particle selection and filtering. In general smaller particles are more desirable for thin films of a few microns thick to achieve statistically dispersed distribution of fine particles because relatively fine size of the second phase particles compared to the nickel matrix is an important criterion and characteristic for dispersion strengthening mechanism. By hindering dislocations and forcing them to climb and cross-slip [9], such fine particles are more capable of enhancing the mechanical strength of the thin film. However, on the other hand, the EDXTM at different locations on the cross section of the nickel cordierite film are examined and show similar relative content of cordierite and nickel. This is evident in Figure 3, which indicates that a certain amount of smaller cordierite particles are still well dispersed within the nickel composite film.

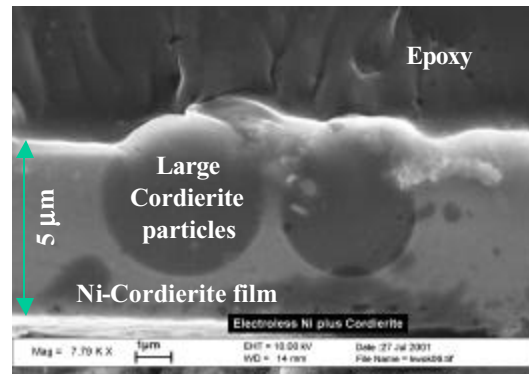


Figure 2. SEM of a 5µm Ni-Cordierite thin film grown on a silicon substrate. There is a distribution of cordierite particle sizes from tens of nm to 5µm.

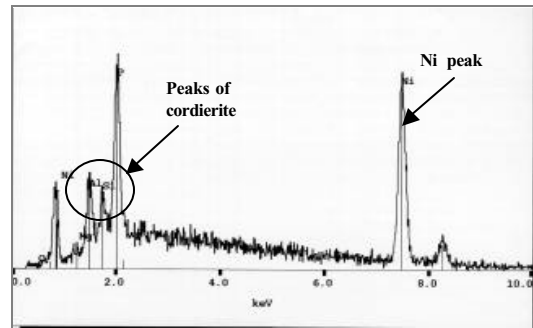


Figure 3. The EDXTM picture shows the composition of the film. The consistency of the relative magnitude of the peak at several locations on the film indicates that the particles are well distributed in the film.

The linear *Rules of Mixtures* [2,6] allows for the computation of physical properties, such as the coefficient of thermal expansion and Young's modulus, of a composite material. According to the rule, the property of a composite film (E_{eff}) has an upper-bound value that can be estimated as,

$$E_{eff} = E_c f_c + E_m f_m \quad (2)$$

as well as a lower-bound value that can be approximated as,

$$E_{eff} = \frac{E_m E_c}{f_c E_m + f_m E_c} \quad (3)$$

Where E_c , E_m , f_c , f_m are the physical parameters and the volume fraction of the ceramic and metal, respectively.

Thus, as cordierite, which has a compatible CTE (3.2 ppm·K⁻¹) with silicon (2.6 ppm·K⁻¹) that is several times smaller than nickel (12~17 ppm·K⁻¹), is being added into the nickel film. lower thermal expansion coefficient of nickel cordierite can be expected. Figures 4(a) and 4(b) juxtapose the post-annealed states of a pure nickel film and a nickel-cordierite film of 5 µm thick. As shown, under a tremendous amount of compressive stress, the electroless nickel film peels off completely from the substrate surface after annealing at 400°C in an inert N₂ environment. On the contrary, the nickel-cordierite film remains relatively intact even after annealing, and adheres well to the silicon. Prior to annealing, a simple adhesion test of applying cellophane tape onto both samples has been performed to confirm that good adhesion exists in both interfaces of nickel-

to-silicon and nickel-cordierite-to-silicon. Therefore, this observation suggests that the relative

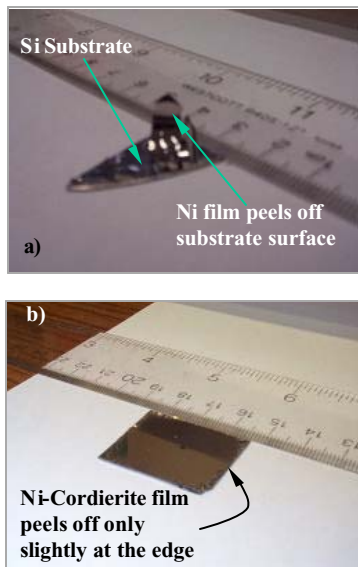


Figure 4. (a) and (b) show the post-annealed state of a nickel film and a nickel-cordierite film on silicon substrates, respectively. As illustrated, the addition of cordierite particles significantly decreases the thermal mismatch between nickel film and silicon substrate.

integrity of nickel-cordierite-to-silicon interface as compared to nickel-to-silicon interface, is mainly due to the presence of cordierite that effectively reduces the thermal stresses. The inclusion of cordierite particles could significantly reduce the CTE mismatch between the silicon substrate and pure nickel film, which is an important consideration in CMOS-integrated, high-precision MEMS, such as a microresonator, gyroscope, and scanning micromirror.

Figure 5 compares the Young's modulus of 2 μ m thick nickel and nickel-cordierite films in their pre- and post-annealed states. The Young's modulus is measured by means of a nanoindentation test using a Nano Indentor® XP from MTS Systems Corporation. Cordierite, an aluminum-magnesium-silicate ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) compound, has a slightly lower Young's modulus ($\sim 128\text{GPa}$) [10] relative to electroless nickel ($\sim 174\text{GPa}$). It can be expected that the composite material will have a slightly lower Young's Modulus, based on the *Rules of Mixture* [2,6]. The volume fraction of the cordierite present in the thin film is estimated to be in the range of 11%~14% at a Young's modulus of 167GPa. Since the density of cordierite (2600 kgm^{-3}) is smaller than nickel (8070 kgm^{-3}), the effective ratio of Young's modulus to density of the composite film, in fact, can be increased by up to 5% in comparison with pure silicon, which is good when the film is used for micro resonating device. By varying the amount of particles present inside the film, the film property will be changed accordingly. Further investigation on the relationship between the particle concentration and film properties will be necessary.

Figure 6 illustrates the effect of cordierite particles on the hardness of the thin film. As shown, prior to annealing, the Berkovich hardnesses of both nickel and nickel-cordierite films

are similar at 7.7 GPa and 7.6 GPa, respectively, based on the nanoindentation results. The inclusion of cordierite

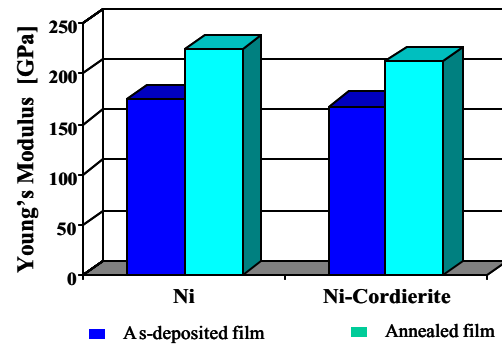


Figure 5. Comparison of the Young's modulus of pure nickel and nickel-cordierite films in their pre- and post-annealed states.

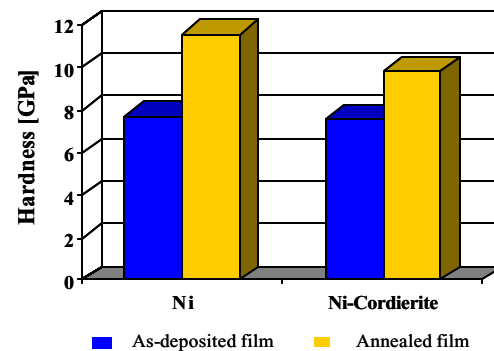


Figure 6. Comparison of the Berkovich hardness of nickel and nickel-cordierite films in their pre- and post-annealed states.

seemingly has no huge effect but lowers the hardness slightly. However, when annealing at 400°C is being carried out, the hardness of nickel increases to 11.6 GPa whereas that of nickel-cordierite elevates to 9.8 GPa. The increase in hardness is due to the precipitation of an intermetallic phase Ni_3P , and the increase in grain size [5]. The precipitation hardening effect might be due to the possibly denser spatial arrangement of fine Ni_3P phase which increases the hardness of electroless nickel film to a greater extent than what cordierite is capable of.

We also measured the resistivity of the pure nickel film and the nickel-cordierite film. Figure 7 compares the resistivity of the films in their pre-annealed and post-annealed states. It was discovered that the incorporation of cordierite particles does not compromise the resistivity of the composite material. Hence, it might be inferred that, below a certain threshold concentration, cordierite particles can have negligible effects on the resistivity of the composite thin film, which is good for application as a MEMS structural material.

Finally, in addition to the CTE, the ferromagnetic property of electroless nickel film can also be enhanced by incorporating Fe(II,III) oxide powders. Figure 8 shows the SEM of a 2 μ m thick Ni-Fe(II,III) oxide composite film identified through EDXTM. Base on the measurement of the magnetic moment vs. magnetic field curves as illustrated in Figure 9, which shows the tremendous improvement of the coercivity of electroless nickel of up to 170 Oe by the addition of Fe(II,III)

oxide, it is evident that Fe(II,III) can be easily co-deposited onto a nickel film and modify its magnetic property.

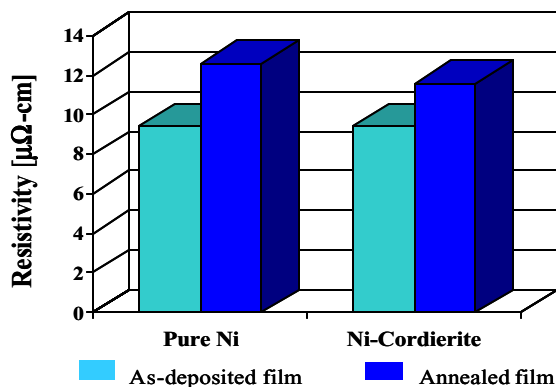


Figure 7. Comparison of the electrical resistivity values of nickel and nickel-cordierite film in their pre-and post-annealed states. The incorporation of ceramic particles into the nickel matrix clearly does not compromise the conductivity of the thin film.

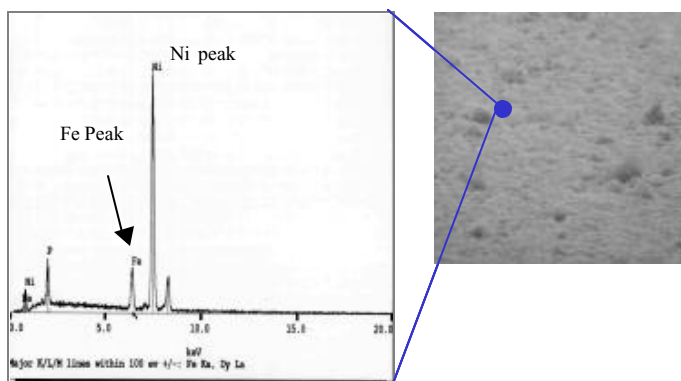


Figure 8. The EDX picture and SEM of a Ni-Fe(II,III) oxide film.

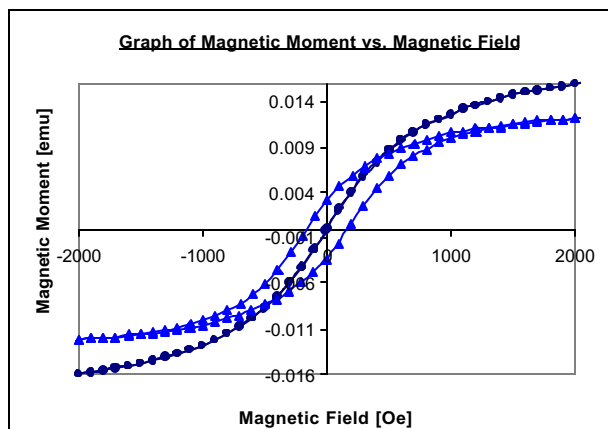


Figure 9. Comparison of the ferromagnetic properties of nickel and Ni-Fe(II,III) oxide composite films. The addition of Fe(II, III) oxide particles increases the coercivity of the nickel film for up to 170 Oe.

CONCLUSIONS

We have successfully demonstrated an easily implemented, highly selective, low temperature, and hence CMOS-compatible method for depositing nickel-ceramic composite

thin film on silicon substrate. Based on the results of annealing, the film deposited has compatible coefficient of thermal expansion with silicon, hence it minimizes the thermal mismatch between pure nickel and silicon. Besides, there was no observable deterioration of the Young's Modulus, hardness and resistivity of nickel with the addition of cordierite particles via electroless plating. Finally, one could also selectively co-deposit magnetic particles with electroless nickel to create magnetic films. Based on these characterizations, we believe this new fabrication technique can provide nickel film with desirable properties and patterns, and allow for cost-efficient batch-fabrication of high-aspect ratio MEMS devices.

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